

REPORT DOCUMENTATION PAGE

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6. AUTHORS J.S. Moore, P. Braun, C. Bielawski, S. Craig, T. Martinez, N. Sottos		5d. PROJECT NUMBER		
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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Illinois - Urbana Board of Trustees of the University of Illinois 1901 S First Street Champaign, IL 61820 -7473		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
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14. ABSTRACT Progress during the prior funding period includes understanding of fracture-induced mechanophore activation, development of a new computational model for predicting mechanochemical phenomena, and the development of new analytical techniques to study mechanochemistry. These studies are making it possible to compare the theoretical and experimental threshold forces that induce mechanochemistry. Other mechanophore advances include a detailed structure-activity relationship for a series of cyclobutane mechanophores and force-induced				
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c. THIS PAGE UU				19b. TELEPHONE NUMBER 217-244-5289

Report Title

ABSTRACT

Progress during the prior funding period includes understanding of fracture-induced mechanophore activation, development of a new computational model for predicting mechanochemical phenomena, and the development of new analytical techniques to study mechanochemistry. These studies are making it possible to compare the theoretical and experimental threshold forces that induce mechanochemistry. Other mechanophore advances include a detailed structure-activity relationship for a series of cyclobutane mechanophores and force-induced Diels-Alder cycloreversions. Experimental methods have been developed to characterize the mechanisms of macroscopic force transfer from a bulk solid polymer to linked mechanophores based on studies that address mechanochemical activation under tensile loading, shear, and fracture behavior.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

05/20/2013 27.00 J. N. Brantley, K. M. Wiggins, C. W. Bielawski. Unclicking the Click: Mechanically Facilitated 1,3-Dipolar Cycloreversions, *Science*, (09 2011): 0. doi: 10.1126/science.1207934

05/20/2013 43.00 Brett A. Beiermann, Sharlotte L.B. Kramer, Jeffrey S. Moore, Scott R. White, Nancy R. Sottos. Role of Mechanophore Orientation in Mechanochemical Reactions, *ACS Macro Letters*, (01 2012): 163. doi: 10.1021/mz2000847

05/20/2013 42.00 Koushik Ghosh, Jeffrey S. Moore. Foldamer Structuring by Covalently Bound Macromolecules, *Journal of the American Chemical Society*, (12 2011): 19650. doi: 10.1021/ja2087163

05/20/2013 41.00 Matthew J. Kryger, Alexander M. Munaretto, Jeffrey S. Moore. Structure–Mechanochemical Activity Relationships for Cyclobutane Mechanophores, *Journal of the American Chemical Society*, (11 2011): 18992. doi: 10.1021/ja2086728

05/20/2013 40.00 Zachary S. Kean, Ashley L. Black Ramirez, Yufan Yan, Stephen L. Craig. Bicyclo[3.2.0]heptane Mechanophores for the Non-scissile and Photochemically Reversible Generation of Reactive Bis-enones, *Journal of the American Chemical Society*, (08 2012): 0. doi: 10.1021/ja3063666

05/20/2013 38.00 Zachary S. Kean, Ashley L. Black Ramirez, Stephen L. Craig. High mechanophore content polyester-acrylate ABA block copolymers: Synthesis and sonochemical activation, *Journal of Polymer Science Part A: Polymer Chemistry*, (09 2012): 3481. doi: 10.1002/pola.26148

05/20/2013 37.00 Hope M. Klukovich, Zachary S. Kean, Ashley L. Black Ramirez, Jeremy M. Lenhardt, Jiaxing Lin, Xiangqian Hu, Stephen L. Craig. Tension Trapping of Carbonyl Ylides Facilitated by a Change in Polymer Backbone, *Journal of the American Chemical Society*, (06 2012): 0. doi: 10.1021/ja302996n

05/20/2013 36.00 Zachary S. Kean, Stephen L. Craig. Mechanochemical remodeling of synthetic polymers, *Polymer*, (02 2012): 1035. doi: 10.1016/j.polymer.2012.01.018

05/20/2013 35.00 Ashley L. Black Ramirez, James W. Ogle, Andrew L. Schmitt, Jeremy M. Lenhardt, Matthew P. Cashion, Mahesh K. Mahanthappa, Stephen L. Craig. Microstructure of Copolymers Formed by the Reagentless, Mechanochemical Remodeling of Homopolymers via Pulsed Ultrasound, *ACS Macro Letters*, (01 2012): 23. doi: 10.1021/mz200005u

05/20/2013 34.00 Hope M. Klukovich, Zachary S. Kean, Scott T. Iacono, Stephen L. Craig. Mechanically Induced Scission and Subsequent Thermal Remending of Perfluorocyclobutane Polymers, *Journal of the American Chemical Society*, (11 2011): 17882. doi: 10.1021/ja2074517

05/20/2013 33.00 Charles E. Diesendruck, Brian D. Steinberg, Naoto Sugai, Meredith N. Silberstein, Nancy R. Sottos, Scott R. White, Paul V. Braun, Jeffrey S. Moore. Proton-Coupled Mechanochemical Transduction: A Mechanogenerated Acid, *Journal of the American Chemical Society*, (08 2012): 12446. doi: 10.1021/ja305645x

05/20/2013 32.00 Aaron C. Jackson, Jonathan A. Bartelt, Paul V. Braun. Transparent Self-Healing Polymers Based on Encapsulated Plasticizers in a Thermoplastic Matrix, *Advanced Functional Materials*, (12 2011): 4705. doi: 10.1002/adfm.201101574

05/20/2013 31.00 Johnathan N. Brantley, Sai Sriharsha M. Konda, Dmitrii E. Makarov, Christopher W. Bielawski. Regiochemical Effects on Molecular Stability: A Mechanochemical Evaluation of 1,4- and 1,5-Disubstituted Triazoles, *Journal of the American Chemical Society*, (06 2012): 9882. doi: 10.1021/ja303147a

05/20/2013 30.00 Kelly M. Wiggins, Johnathan N. Brantley, Christopher W. Bielawski. Polymer Mechanochemistry: Force Enabled Transformations, *ACS Macro Letters*, (05 2012): 0. doi: 10.1021/mz300167y

05/20/2013 29.00 Kelly M. Wiggins, Christopher W. Bielawski. A Mechanochemical Approach to Deracemization, *Angewandte Chemie International Edition*, (02 2012): 0. doi: 10.1002/anie.201107937

05/20/2013 28.00 Sai Sriharsha M. Konda, Johnathan N. Brantley, Christopher W. Bielawski, Dmitrii E. Makarov. Chemical reactions modulated by mechanical stress: Extended Bell theory, *The Journal of Chemical Physics*, (10 2011): 0. doi: 10.1063/1.3656367

08/23/2011 9.00 Cassandra M. Kingsbury, Preston A. May, Douglas A. Davis, Scott R. White, Jeffrey S. Moore, Nancy R. Sottos. Shear activation of mechanophore-crosslinked polymers, *Journal of Materials Chemistry*, (02 2011): 8381. doi: 10.1039/c0jm04015k

08/23/2011 20.00 Corissa K. Lee, Douglas A. Davis, Scott R. White, Jeffrey S. Moore, Nancy R. Sottos, Paul V. Braun. Force-Induced Redistribution of a Chemical Equilibrium, *Journal of the American Chemical Society*, (10 2010): 16107. doi: 10.1021/ja106332g

08/23/2011 19.00 Kelly M. Wiggins, Jay A. Syrett, David M. Haddleton, Christopher W. Bielawski. Mechanically Facilitated Retro [4 + 2] Cycloadditions, *Journal of the American Chemical Society*, (05 2011): 7180. doi: 10.1021/ja201135y

08/23/2011 18.00 Dong Wu, Jeremy M. Lenhardt, Ashley L. Black, Boris B. Akhremtchev, Stephen L. Craig. Molecular Stress Relief through a Force-Induced Irreversible Extension in Polymer Contour Length, *Journal of the American Chemical Society*, (11 2010): 15936. doi: 10.1021/ja108429h

08/23/2011 17.00 Jeremy M. Lenhardt, James W. Ogle, Mitchell T. Ong, Robert Choe, Todd J. Martinez, Stephen L. Craig. Reactive Cross-Talk between Adjacent Tension-Trapped Transition States, *Journal of the American Chemical Society*, (03 2011): 3222. doi: 10.1021/ja107645c

08/23/2011 16.00 Andrew G. Tennyson, Kelly M. Wiggins, Christopher W. Bielawski. Mechanical Activation of Catalysts for C?C Bond Forming and Anionic Polymerization Reactions from a Single Macromolecular Reagent, *Journal of the American Chemical Society*, (11 2010): 16631. doi: 10.1021/ja107620y

08/23/2011 15.00 Jeremy M. Lenhardt, Ashley L. Black, Brett A. Beiermann, Brian D. Steinberg, Faiyam Rahman, Tasha Samborski, Joseph Elsakr, Jeffrey S. Moore, Nancy R. Sottos, Stephen L. Craig. Characterizing the mechanochemically active domains in gem-dihalocyclopropanated polybutadiene under compression and tension, *Journal of Materials Chemistry*, (02 2011): 8454. doi: 10.1039/c0jm04117c

08/23/2011 14.00 Ashley L. Black, Joshua A. Orlicki, Stephen L. Craig. Mechanochemically triggered bond formation in solid-state polymers, *Journal of Materials Chemistry*, (02 2011): 8460. doi: 10.1039/c0jm03875j

08/23/2011 13.00 Kelly M. Wiggins, Todd W. Hudnall, Andrew G. Tennyson, Christopher W. Bielawski. Selective scission of pyridine–boronium complexes: mechanical generation of Brønsted bases and polymerization catalysts, *Journal of Materials Chemistry*, (01 2011): 8355. doi: 10.1039/c0jm03619f

08/23/2011 12.00 Ashley L. Black, Jeremy M. Lenhardt, Stephen L. Craig. From molecular mechanochemistry to stress-responsive materials, *Journal of Materials Chemistry*, (11 2010): 1655. doi: 10.1039/c0jm02636k

08/23/2011 11.00 Mitchell T. Ong, Susan A. Odom, Nancy R. Sottos, Scott R. White, Todd J. Martinez, Jeffrey S. Moore, Matthew J. Kryger. Masked Cyanoacrylates Unveiled by Mechanical Force, *Journal of the American Chemical Society*, (04 2010): 4558. doi: 10.1021/ja1008932

08/23/2011 10.00 Nancy R. Sottos, Scott R. White, Douglas A. Davis, Sharlotte L. B. Kramer, Jeffrey S. Moore, Brett A. Beiermann. Environmental effects on mechanochemical activation of spiropyran in linear PMMA, *Journal of Materials Chemistry*, (02 2011): 8443. doi: 10.1039/c0jm03967e

08/24/2011 25.00 J. M. Lenhardt, M. T. Ong, R. Choe, C. R. Evenhuis, T. J. Martinez, S. L. Craig. Trapping a Diradical Transition State by Mechanochemical Polymer Extension, *Science*, (08 2010): 1057. doi: 10.1126/science.1193412

08/26/2013 44.00 Johnathan N. Brantley, Constance B. Bailey, Kelly M. Wiggins, Adrian T. Keatinge-Clay, Christopher W. Bielawski. Mechanobiochemistry: harnessing biomacromolecules for force-responsive materials, *Polymer Chemistry* , (03 2013): 3916. doi: 10.1039/c3py00001j

08/26/2013 46.00 Kelly M Wiggins, Christopher W Bielawski, Johnathan N Brantley. Polymer mechanochemistry: the design and study of mechanophores, *Polymer International*, (01 2013): 2. doi: 10.1002/pi.4350

08/28/2008 2.00 S.L. Potisek, D.A. Davis, N.R. Sottos, S.R. White, J.S. Moore. Mechanophore-Linked Additional Polymers, *Journal American Chemical Society*, (): . doi:

08/28/2008 3.00 C.R. Hickenboth, J.D. Rule, J.S. Moore. Preparation of endine-crosslinked networks and their reactivity under thermal and mechanical conditions, *Tetrahedron*, (): . doi:

08/28/2008 4.00 J.P. Youngblood, N.R. Sottos. bioinspired materials for self cleaning and self healing, *MRS Bulletin*, (): . doi:

08/28/2008 5.00 H.M. Anderson, M.W. Keller, J.S. Moore, N.R. Sottos, S.R. White. Self Healing Polymers and Composites , (): . doi:

TOTAL: 35

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

05/20/2013 39.00 Stephen L. Craig. Mechanochemistry: A tour of force, *Nature*, (07 2012): 176. doi: 10.1038/487176a

08/24/2011 26.00 J.S. Moore, N.R. Sottos. Spot-on healing, *Nature*, (04 2011): 299. doi:

TOTAL: 2

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Bielawski:

Brantley, J. N. "Beyond the Thermal Limit: Novel Mechanochemical Reactivity". Milliken Graduate Research Symposium, Spartanburg, SC. May 2013.

Brantley, J. N. "Breaking the Limit: New Insights into Mechanochemical Phenomena". University of Texas, Austin, TX. February 2013.

Bielawski, C. W. Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea, June 4, 2013

Bielawski, C. W. MIT, Merck-Karl Pfister Lectures, October 17, 2012

Bielawski, C. W. Northwestern University, May 17, 2013

Bielawski, C. W. Kangwon National University, Chun Cheon, South Korea, May 2, 2013

Bielawski, C. W. Oak Ridge National Laboratory, April 19

Bielawski, C. W. University of Tennessee, Knoxville, April 18, 2013

Bielawski, C. W. Keynote Lecturer, 11th Quebec Center for Self-Assembled Chemical Structures Annual Meeting, McGill University, Montreal, Canada, May 9, 2013

Bielawski, C. W. Ewha Womens University, Seoul, Korea, March 21, 2013

Bielawski, C. W. Seoul National University, March 14, 2013

Bielawski, C. W. Plenary Lecturer, Zing Polymer Conference, Xcaret Eco Park, Mexico, November 15, 2012

Bielawski, C. W. Plenary Lecturer, Journal of Polymer Science Innovation Award Symposium, 244th ACS National Meeting, Philadelphia, PA, August 20, 2012

Braun:

"Mechanochemistry in Polymer and Composite Materials," 2012 Symposium on Stimuli-Responsive Materials, Sonoma, CA, October 2012

"Self-Healing and Mechanochromic Coatings," University of Minnesota, Minneapolis, MN, January 2013

Craig:

"Mechanochemical Remodeling of Synthetic Polymers", Milliken Corp., Spartanburg, SC, June 18, 2013.

"From Trapped Transition States to Self-Healing Polymers", Department of Chemistry, Colby College, April 12, 2013.

"From Trapped Transition States to Self-Healing Polymers", Department of Chemistry, University of Cincinnati, Cincinnati, OH, March 8, 2013.

"A Tour of Force: Mechanochemistry for Trapping Transition States and Self-Healing Polymers", Department of Chemistry, University of Virginia, Charlottesville, VA, Feb. 22, 2013.

"Molecular Design of Mechano-Responsive Polymers", Technical University of Eindhoven, Eindhoven, The Netherlands, January, 2013.

"Mechanochemistry: From Trapped Transition States to Self-Healing Polymers", Department of Chemistry, Northwestern University, Evanston, IL, January 24, 2013.

"Molecular Design of Mechano-Responsive Polymers", Macromolecular Materials GRC, Ventura, CA, January 9, 2013.

"Mechanochemical Remodeling: From New Reactions to Adaptive Materials", Oak Ridge National Labs, Oak Ridge, TN, Dec. 11, 2012.

“Mechanochemical Remodeling of Synthetic Polymers”, Bridgestone Tire, Akron, OH, October 16, 2012.

“Mechanochemical Remodeling of Materials and Reaction Pathways”, Department of Chemistry, Davidson College, Davidson, NC, Sept. 21, 2012.

“Mechanochemical Remodeling of Synthetic Polymers”, Lord Corp., Cary, NC, August 20, 2012.

Moore:
University of Wisconsin-Madison, Madison, WI, March 14, 2013, “Mechanoresponsive Materials and Self-Healing Systems.”

University of Iowa, Iowa City, IA, November 2, 2012, “Mechanoresponsive Materials and Self-Healing Systems.”

American Chemical Society Fall Meeting, Philadelphia, PA, August 20, 2012, “Molecular Design and Experimental Testing of Mechanochemical Activity.”

Polymer Networks Group Conference, Jackson Hole, WY, August 14, 2012, “Polymer Networks in Mechanoresponsive Materials and Self-Healing Systems.”

Distinguished Lecturer for 2012 Annual Grantees'/Contractors' Meeting for AFOSR, Arlington, VA, July 30-August 3, 2012, "ARO MURI '07: Mechano-chemically Active Polymer Composites."

May, P.A.; Beiermann, B.A.; Hamoy, M.B.; White, S.R.; Sottos, N.R.; Moore, J.S. “Damage Sensing Polymers: Understanding the Role of Polymer Architecture in Mechanochemical Reactions” Dept. of Chemistry and Biochemistry Seminar Series, Andrews University, Berrien Springs, Michigan, Sep. 2012.

Diesendruck, C.E.; Moore, J.S. “Proton-Coupled Mechanochemical Transduction – Mechanogenerating Acids” Nanohour, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois, Nov. 2012.

May, P.A.; Beiermann, B.A.; Hamoy, M.B.; White, S.R.; Sottos, N.R.; Moore, J.S. “An Increased Throughput Method for Screening Mechanochemical Reactions” Graduate Student Seminar Series, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois, Jan. 2013.

Diesendruck, C.E.; Moore, J.S. “Proton-Coupled Mechanochemical Transduction – Mechanogenerating Acids” The 78th Meeting of the Israel Chemical Society, Tel-Aviv, Israel, Feb 2013

Diesendruck, C.E.; Moore, J.S. “Proton-Coupled Mechanochemical Transduction – Mechanogenerating Acids” Fourth International Conference on Self-Healing Materials, Ghent, Belgium, Jun 2013

Sottos:
N. R. Sottos, International Symposium on Experimental Mechanics, Plenary Lecture, Multiscale Characterization of Autonomous Materials Systems, Taipei, Taiwan, November 8, 2012.

A.N. Celestine, B.A. Beiermann, C.M. Kingsbury, P.A. May, J.S. Moore, N.R. Sottos, S.R. White, Damage Sensing in Mechanophore-Linked, Rubber-Toughened Brittle Polymers, Annual Conference for the Society of Engineering Science, Atlanta, GA October 11, 2012.

M.N. Silberstein, C.M. Kingsbury, B.A. Beiermann, S.B. Kramer. K.Min, L.D. Cremar, T.J. Martinez, N.R. Aluru, S.R. White and N.R. Sottos, Understanding Mechanoresponsive Polymers via Microstructurally-Based Models or Multiscale Modeling for Design of Mechanoresponsive Polymers, XXIII ICTAM, Beijing, China, August 19, 2012.

Number of Presentations: 39.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

09/10/2013 56.00 Silberstein, M.N., Kingsbury, C.M., Min, K., Kramer, S., Beiermann, B., Aluru, N., White, S.R., Sottos, N.R.. Multiscale modeling of mechanoresponsive polymers, 2012 Annual Conference on Experimental and Applied Mechanics. 2013/06/03 01:00:00, . : ,

09/10/2013 57.00 B. Beiermann, S. White, N. Sottos, S. Kramer. Simultaneous observation of phase-stepped photoelastic images using diffraction gratings, the 2012 Annual Conference on Experimental and Applied Mechanics,. 2013/06/03 01:00:00, . : ,

TOTAL: 2

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

ReceivedPaper

03/15/2010 6.00 J. Lenhardt, M. Ong, R. Choe, C. Evenhuis, T. Martinez, S. Craig. Contraction by Extension and Tension Trapping of a Transition State in a Mechanochemical Isomerization, (03 2010)

08/09/2008 1.00 M.J. Serpe, F.R. Kersey, J.R. Whitehead, S.L. Craig. A Simple and Practical Spreadsheet-Based Method to Extract Single-Molecule Dissociation Kinetics from Variable Loading-Rate Force Spectroscopy Data, ()

08/24/2011 22.00 J. N. Brantley, K. M. Wiggins, C.W. Bielawski. Un-clicking the Click: Mechanically-Facilitated 1,3-Dipolar Cycloreversions, Science (08 2011)

08/24/2011 23.00 Aaron C. Jackson, Jonathan A. Bartelt, Paul V. Braun. Transparent Self-healing Polymers based on Encapsulated Plasticizers in a Thermoplastic Matrix, Advanced Functional Materials (08 2011)

TOTAL: **4**

Number of Manuscripts:**Books**ReceivedPaper

08/24/2011 24.00 P.V. Braun. Self-Healing Polymers, not applicable: John Wiley and Sons, Inc., (09 2010)

TOTAL:**1****Patents Submitted****Patents Awarded****Awards**

C. Bielawski:

Merck-Karl Pfister Visiting Professorship, MIT

Milliken Graduate Research Lecturer (to J. N. Brantley)

Craig:

Endowed Distinguished Chair (Duke): William T. Miller Professor

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>	Discipline
Johnathan Brantley	1.00	
Kelly Wiggins	1.00	
Brett Beiermann	1.00	
Asha-Dee Celestine	1.00	
Preston May	1.00	
Corissa Lee	1.00	
FTE Equivalent:	6.00	
Total Number:	6	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
Meredith Silberstein (Beckman Fellow)	0.00
Charles Diesendruck	1.00
Kristopher Wynant	0.50
FTE Equivalent:	1.50
Total Number:	3

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>	National Academy Member
Stephen Craig	0.02	
FTE Equivalent:	0.02	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Yifei Wang (March 2013)

Total Number:

1

Names of personnel receiving PHDs

NAME

Kelly Wiggins

Ashley Ramirez

Brett Beiermann

Corissa Lee

Total Number:

4

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

Erica Malloch	0.13
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Ashley Trimmell	0.23
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Jiping Yang (Visiting Scholar)	0.00
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Jinyun Liu (Visiting Scholar)	0.44
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Aeri Lee (Visiting Scholar)	0.00
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FTE Equivalent:	0.80
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Total Number:	5
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Sub Contractors (DD882)

1 a. Duke University

1 b. 2200 West Main Street

Suite 710

Durham

NC

277054010

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e):

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

1 a. Duke University

1 b. Office of Sponsored Programs

Box 90491

Durham

NC

277080491

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e):

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

1 a. Stanford University

1 b. Office of Sponsored Research

340 Panama Street

Stanford

CA

943054100

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e):

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

1 a. Stanford University

1 b. Mail Stop 4125, Room 110

651 Serra Street

Stanford

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943057212

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e):

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

1 a. The University of Texas at Austin

1 b. 10000 Burnet Road

Austin

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787584423

Sub Contractor Numbers (c): 2007-00748-02

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e):

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

1 a. The University of Texas at Austin

1 b. 10000 Burnet Road

Austin

TX

787584423

Sub Contractor Numbers (c): 2007-00748-02

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e):

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

Inventions (DD882)

Scientific Progress

see attachment

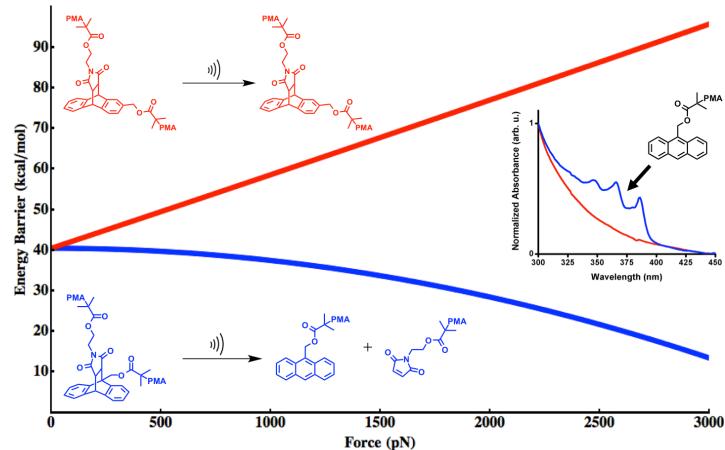
Technology Transfer

Bielawski:

Overview. Research efforts in the Bielawski laboratory have focused on (1) the implementation of computational modeling in the *a priori* design of mechanically-responsive polymeric materials, with an emphasis on developing novel classes of polymeric networks that resist damage under the action of exogenous forces; and (2) the development of new classes of stress-responsive biocomposites that contain mechanically labile biomolecules.

Mechanical Suppression of Chemical Reactivity.

We previously reported¹ a new computational model that may be used to predict mechanochemical reactivity. Our theory (*i.e.*, Extended Bell Theory (EBT)) modifies the classic Bell-Zhurkov formula² to more rigorously account for force-induced shifts in transition and reactant states along a given mechanical reaction coordinate in the full multidimensional configuration space of the molecule of interest. EBT incorporates higher-order effects that arise from 1) the elastic energy stored in a molecule as a result of mechanical deformation and 2) the additional work performed by the applied force as a result of molecular distortion. These effects (which



Rate of scission in high M_n materials ($M_n = 88$ kDa; $M_n = 71$ kDa)

Figure 1. EBT predicted that Diels-Alder adducts derived from 2-substituted anthracene derivatives (red) would not be susceptible to mechanical cycloreversion; adducts derived from 9-substituted anthracene moieties, however, were predicted to undergo mechanical cycloreversion (blue). Ultraviolet-visible spectroscopy revealed that ultrasound irradiation (5 h; 6–9 °C) of acetonitrile solutions (10 mg mL⁻¹) of poly(methyl acrylate) materials containing both congeners only induced cycloreversion in the case of the latter (inset). Ultraviolet-visible spectra were acquired in tetrahydrofuran with polymer concentrations of 10 mg mL⁻¹. Kinetic analyses of high molecular weight materials revealed that the rate of chain scission was two orders of magnitude higher for materials containing adducts derived from 9-substituted anthracene. Adapted from Ref. 3

ultimately stem from the force constants associated with all of the bonds in the molecule of interest) can quickly be extracted from unconstrained geometry optimizations and saddle point searches; thus, our theory quickly and efficiently analyses how forces will influence the activation barrier for a given transformation. An important consequence of the multidimensional energy surface associated with mechanochemical transformations is that mechanical stress can either accelerate or suppress chemical reactivity (Figure 1).³ The mechanical suppression of reactivity is an overlooked phenomenon in the field of mechanochemistry, despite the myriad applications that could arise from the ability to selectively retard a given chemical process (*e.g.*, polymeric materials that are designed to resist mechanical damage when stressed). Guided by our computational model, we focused on exploring the suppression of the formal [4+2] cycloreversion of a Diels-Alder adduct derived from anthracene and maleimide (Figure 1).³ We selected this system for two primary reasons: 1) the subtle change in molecular architecture was predicted to drastically alter the associated mechanochemical reactivity (as compared to a related system we previously reported;⁴ *cf* blue molecules in Figure 1), a counterintuitive prediction based on the chemical similarity between the two congeners, and 2) no reaction acceleration at any force was predicted, which would allow us to observe reaction suppression under experimentally relevant conditions. As Figure 1 shows, extended ultrasound irradiation of acetonitrile solutions of poly(methyl acrylate) chains containing the mechanically inert cycloadduct did not result in the formation of detectable amounts of anthracene-terminated polymer fragments (as determined by ultraviolet-visible spectroscopy). Moreover, kinetic analyses revealed that the rates of chain scission in high molecular weight materials containing

the mechanically inert congener were two orders of magnitude lower than the analogous rates for materials containing the mechanically labile adduct.

Novel Stress-Sensing Biocomposites. The preparation of mechanically responsive chemical functionalities (*i.e.*, mechanophores^{5,6}) often involves tedious chemical syntheses. As a consequence, the precise and rapid tuning of mechanochemical reactivity (*e.g.*, through chemical modifications of existing mechanophore scaffolds) can be rather challenging. Our recent efforts have focused on harnessing the biosynthetic machinery of living organisms to quickly access a variety of mechanically sensitive biomolecules (*i.e.*, biomechanophores⁷) that exhibit diverse activity under the action of mechanical forces. As shown in Figure 2, we envisaged that the mechanical modulation of the photophysical properties of two fluorescent protein variants could afford access to distinct stress reporters: 1) a ratiometric stress sensor derived from reversibly shifting the λ_{em} of polymeric materials containing an enhanced yellow fluorescent protein (eYFP), and 2) an intensiometric stress sensor derived from mechanical fluorescence quenching of polymeric materials containing a genetically modified green fluorescent protein (GFPuv).⁸ Importantly, poly(methyl methacrylate) biocomposite materials could easily be prepared by adding the fluorescent proteins directly to the bulk polymerization of methyl methacrylate. Mechanical compression of composites containing eYFP resulted in a gradual, hypsochromic shift in λ_{em} under increasing force (Figure 2). Moreover, the λ_{em} was bathochromically shifted to the pre-compression value *via* thermal annealing at 40 °C for 2 h. The λ_{em} of the annealed material could subsequently be shifted *via* mechanical compression. Compression of materials containing the modified GFPuv also resulted in the anticipated fluorescence quenching (Figure 2). Additionally, fluorescence intensity was found to decrease monotonically with increasing force, a hallmark of mechanical activations in bulk materials.

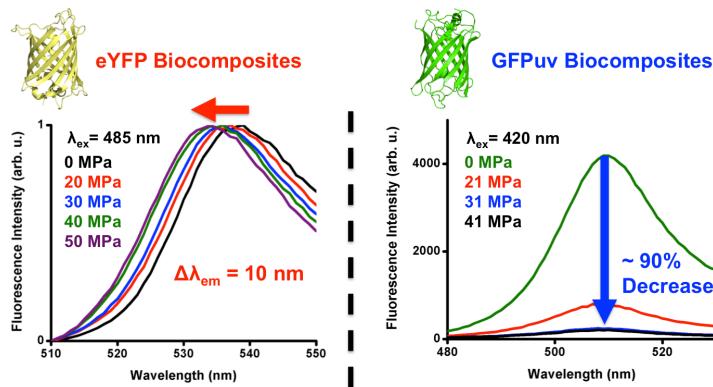


Figure 2. (Left) eYFP-containing biocomposites were prepared by adding eYFP directly to the homopolymerization of methyl methacrylate. Compression of the resulting materials resulted in a gradual hypsochromic shift in the maximal fluorescence emission. Normalized fluorescence spectra are shown. (Right) GFPuv-containing biocomposites were prepared by adding a GFPuv mutant directly to the homopolymerization of methyl methacrylate. Compression of the resulting materials resulted in a nearly 90% reduction in fluorescence intensity. Figure adapted from Ref. 8

Future Efforts. Future directions in the Bielawski group will continue to focus on probing the mechanical suppression of chemical reactivity. Specifically, we are seeking experimental evidence in support of so-called “molecular catch bonds”,³ or molecules that resist degradation *via* covalent bond scission with increasing force until a threshold force is reached, after which the molecule will undergo controlled bond scission. Such systems are extremely rare, and have only recently been implicated in non-biochemical contexts.⁹ Direct experimental measurement of molecular catch bonds in polymeric materials has yet to be realized. Apart from their fundamental importance, the discovery of molecular catch bonds could provide insight into the interplay between macroscopic forces and their effects at the molecular level, as well as facilitate the preparation of next-generation stress sensors with highly tuned force sensitivities. We also have a continued interest in the development of “catalytic” polymer mechanochemistry.¹⁰ By employing dynamic covalent chemistry, we envision that polymers can be attached to functionalities *in situ* to facilitate mechanochemical transformations and

subsequently be selectively cleaved to complete the catalytic cycle. In addition to improving the atom economy of various mechanochemical processes, “catalytic” mechanochemistry could also render large-scale mechanical synthesis more feasible. Finally, we intend to continue exploring the design of new biomechanophore scaffolds such as mechanically labile enzyme scaffolds that could allow us to precisely modulate the selectivity and/or activity of these biochemical catalysts for applications in materials science and chemical synthesis.

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Braun:

Over the reporting period, we made two significant mechanochemistry advances, and initiated research on the promising concept of swelling induced mechanochemistry. In the first advance, spiropyran (SP) mechanophore was synthesized into the soft or hard phase of segmented polyurethanes (SPU) and used as a molecular probe of force and orientation. Upon either tensile stretching or irradiation with UV light the SP-linked segmented polyurethane (SP-SPU) adopt a deep purple coloration and are fluorescent, demonstrating the force and UV-induced formation of the open merocyanine (MC) form of the mechanophore. Order parameters calculated from the anisotropy of the fluorescence polarization of merocyanine (MC) were used to characterize the orientation in each phase. Exploiting the ability of SP to be force activated, the SP-SPUs were also mechanically activated to track the force and orientation in each domain of segmented polyurethane during uniaxial tensile loading.

In the second advance, a novel mechanophore with acid-releasing capability is designed to produce a simple catalyst for chemical change in materials under mechanical stress. The mechanophore, based on a gem-dichlorocyclopropanated indene, is synthesized and used as a

cross-linker in poly(methyl acrylate). Force-dependent rearrangement is demonstrated for cross-linked mechanophore samples loaded in compression, while the control shows no significant response. The availability of the released acid is confirmed by exposing a piece of insoluble compressed polymer to a pH indicator solution. The development of this new mechanophore is the first step toward force-induced remodeling of stressed polymeric materials utilizing acid-catalyzed cross-linking reactions.

As a new direction, the SP mechanophore, is used to investigate mechanical forces in crosslinked poly(methyl methacrylate) during swelling with common organic solvents. The spirocyclic is incorporated as a crosslinker. A correlation is observed between polymer swelling and fluorescence intensity, suggesting that the forces during swelling are sufficient to drive the electrocyclic ring-opening reaction of spirocyclic to its colored and fluorescent merocyanine form. Control experiments and solvatochromic studies validate that activation is indeed due to swelling-induced mechanical forces, and not to solvent effects. Systematic studies varying solvents and crosslinking densities provides insight on how these parameters influence mechanical forces at the molecular level during polymer swelling.

Craig:

Major advances (published) include the development of bicyclic mechanophores that provide record amounts of “covalent stress relief” which overstressed within a polymer subchain. The bicycloheptane and bicyclooctanes also unveil latent reactivity that can be used for covalent cross-linking in materials at the point and time of pending failure. Among these mechanophores is a new combination of responsiveness, in which mechanical force activates a mechanophore and light reverses the activation.

The bicyclooctanes are particularly noteworthy in two aspects. First, they are readily scaled into every repeat unit of a high molecular weight polymer – the first example of such high mechanophore content beyond the dihalocyclopropanes developed earlier in the MURI. Second, their mechanical activation results in a distribution of product stereochemistry that can be characterized, and that has been used to enable a level of mechanistic insight into the mechanical mechanism that can be directly compared to theory.

We have also demonstrated a new mechanism by which to regulate mechanochemical activity in polymers: a so-called “polymer lever arm effect.” The polymer backbone has typically been treated as simply a tether by which mechanical force is applied to a mechanophore, but we have shown using single-molecule methods that the role is far more subtle and far more influential. By strategically coupling nuclear motions during a reaction to the geometry of an extended polymer backbone, we are able to induce thousand-fold rate accelerations (in this case at ~nanoNewton forces) that were previously unanticipated.

Finally, we have demonstrated the proof-of-concept of mechanochemical strengthening in response to destructive mechanical forces. Shear forces that literally break polymer chains are partially directed in mechanophore activation, leading to subsequent cross-linking reactions. Remarkably, the number of cross-links formed under destructive shear is large enough to lead to orders-of-magnitude increases in modulus.

Other advances (unpublished) include the first reversible mechanochemical devices, based on PDMS platforms, and coupling mechanical activation to single-molecule conductance experiments for a mechanical “turn on” of conductance.

Martinez:

We have extended our simulations of mechanochemical activation to include large sections of the polymer chain surrounding the mechanophore. The results are largely in agreement with previous simulations focused on the mechanophore itself. We have begun simulations of brominated cyclopropane mechanophore chains, which will allow for detailed comparison of the forces needed to cause mechanophore rupture. Measurements have been made in the Craig lab using AFM pulling, and we will compare our results to these measurements as a detailed test of the force-modified potential energy surface concept. We have also simulated the mechanochemical depolymerization of PPA, following experiments in the Moore group. We find that the depolymerization mechanism is heterolytic and have been able to carry out these simulations with chains containing up to four PPA monomers. These show nearly immediate unzipping of the four-unit "polymer" within a picosecond of the initial force-induced bond cleavage. We are currently investigating the force modified potential energy surface for this depolymerization.

Moore:

Summary

Materials systems with reusable building blocks are attractive for autonomous adaptive structures that have the ability to remodel themselves in response to external stimuli, damage, and environmental conditions. A familiar example of reusable resources found in nature is the recycling of monomeric building blocks for peptide, carbohydrate, and nucleic acid polymers through the process of depolymerization and repolymerization. For synthetic materials, remodeling has the potential to extend device lifetime by removal and replacement of damaged regions or by restructuring parts to meet changing demands of their use. One approach that we envisage in autonomically adaptive polymeric materials involves stimuli-triggered depolymerization followed by mass transfer of the resulting monomer to its newly needed location and subsequent repolymerization. This concept requires the position of a monomer-polymer equilibrium to be switchable, or, alternatively, metastable polymers in which a triggering event activates depolymerization. Polymers above their ceiling temperature (T_c) yet stabilized by end-caps are potential candidates of the latter, where mechanical damage might activate reversion to monomer.

The goal of this research is to develop a synthetic system that can mimic the tissue regeneration processes which occurs in biological systems where material is constantly remodeled through polymerization-depolymerization equilibrium. End-capped poly(o-phthalaldehyde) (PPA) is a metastable polymer with a low ceiling temperature, which can undergo chemically driven depolymerization to produce o-

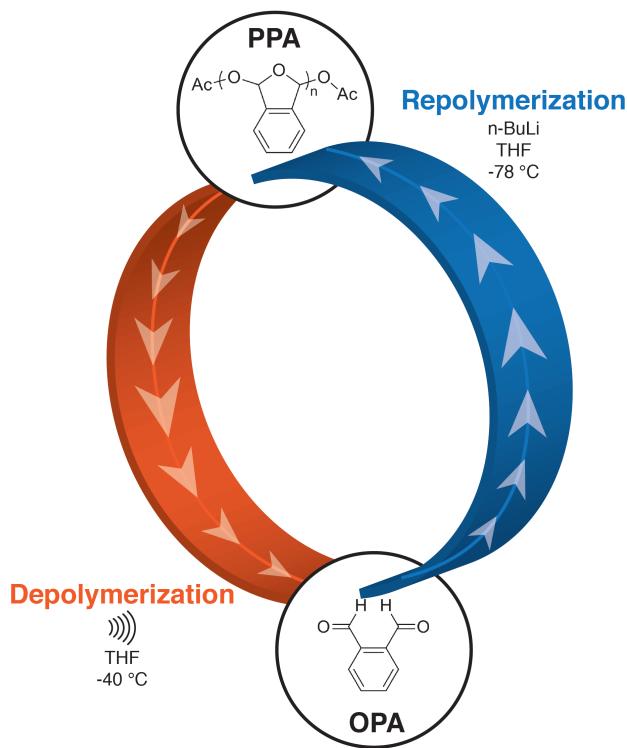


Figure 1. PPA depolymerization to monomer and subsequent chemical repolymerization.

phthalaldehyde monomer. This in turn, can be chemically polymerized to re-make the polymer (figure 1).

In the context of this project, we studied the mechanochemistry of PPA in order to understand how mechanical force may be harnessed to trigger the depolymerization to monomer. The monomer produced by a mechanically triggered depolymerization was reused to regenerate the polymer.

The implications of this work are fundamental toward advancements in autonomic polymer self-healing, where the material is made of recyclable monomer units and provide the mass for the regeneration of a damaged volume.

Progress to Date

High molecular weight PPA was prepared by cationic polymerization. We recently demonstrated that this polymerization produces exclusively cyclic structures; therefore, no removable end groups are present. We prepared a cyclic PPA with 90 kDa as a model compound, as a similar polymer of 26 kDa molecular weight as control. As previously demonstrated by us, below a certain molecular weight threshold, the mechanical force harnessed by a polymer chain is not enough to cause bond scission under elongational flow fields, in this case ultrasonication. We also compared the experiment to a high T_c polymer, poly(methyl acrylate) (PMA) of similar molecular weight, to demonstrate the difference in the polymer scission processes.

The polymers were dissolved in THF to a concentration where no entanglements are expected (1 mg/mL), and pulsed ultrasound (0.5s on, 1.0s off, 8.7 W/cm²) was applied under argon at -15°C. Figure 2a-c shows the gel-permeation chromatograms of aliquots removed from the Suslick cell during the sonication experiment followed by direct injection in the GPC. The expected decrease in molecular weights consequent from mechanochemical bond scission is clearly observed for PPA₉₀ and PMA₁₀₃. A visible difference is the remarkable decrease in the PPA₉₀ peak area, denoting a decrease in polymer concentration with sonication time. The low molecular weight PPA₂₆ shows no significant changes, providing strong evidence that the depolymerization observed for PPA₉₀ is mechanically triggered.

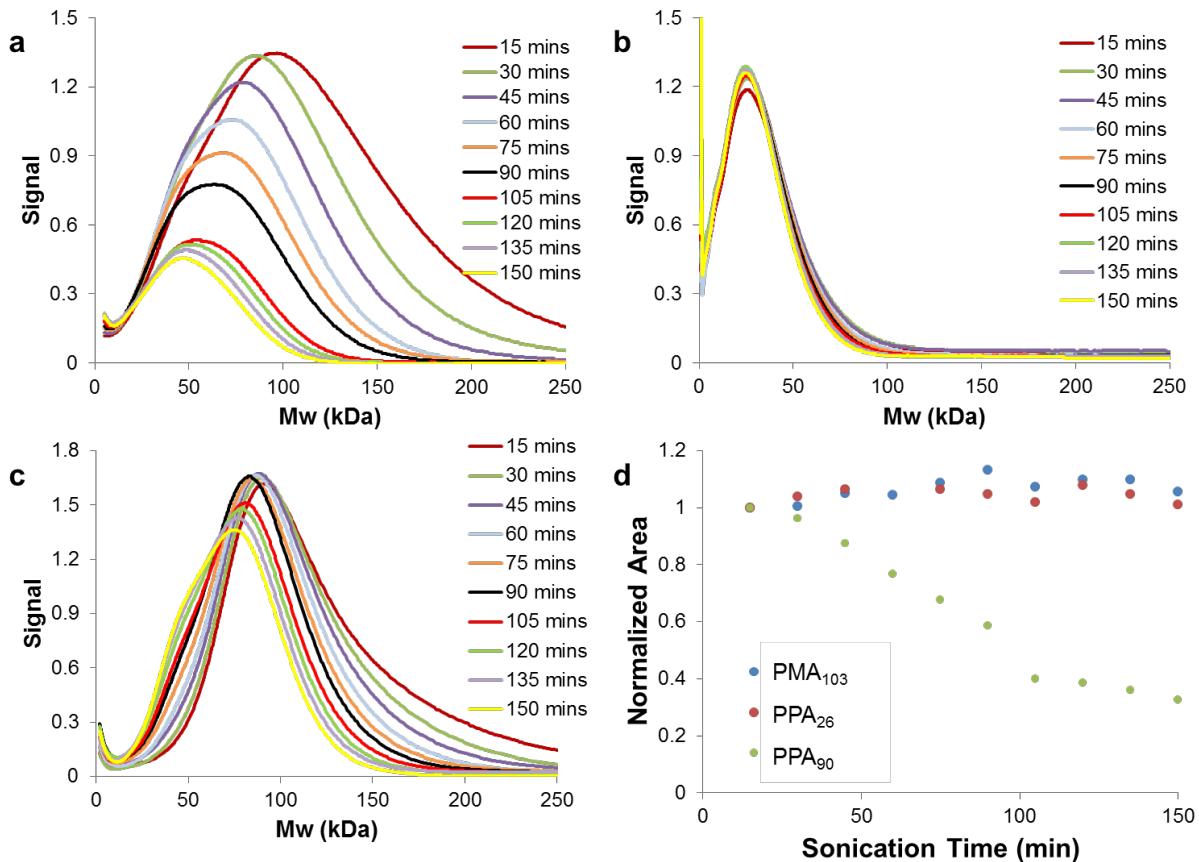


Figure 2. GPC studies of sonicated polymers **a.** PPA₉₀; **b.** PPA₂₆; **c.** PMA₁₀₃ and **d.** change in area ratio with sonication time for PPA₉₀, PPA₂₆ and PMA₁₀₃.

The solution after sonication was added to methanol in order to precipitate out the remaining polymer. The depolymerization products were studied by GC-MS and NMR, confirming the presence of nearly pure *o*-phthalaldehyde monomer.

To test the suitability of this system as a model of a regenerating system, a depolymerization followed by repolymerization was tested. A high molecular weight PPA was sonicated in THF at -40°C. Under these conditions, sonication for 6 hours resulted in around 60% depolymerization of the original polymer, as observed by GPC. Anionic polymerization was then conducted by cooling the reaction mixture to -78°C and adding BuLi as initiator. After 10 hours, the polymer was end-capped by addition of Ac₂O and pyridine. The reaction solution was analyzed by GPC, and two peaks were observed. One peak corresponded to the polymer remaining after sonication, while a new peak appeared, indicating that the produced monomer underwent repolymerization, in this case to a lower molecular weight polymer (figure 3).

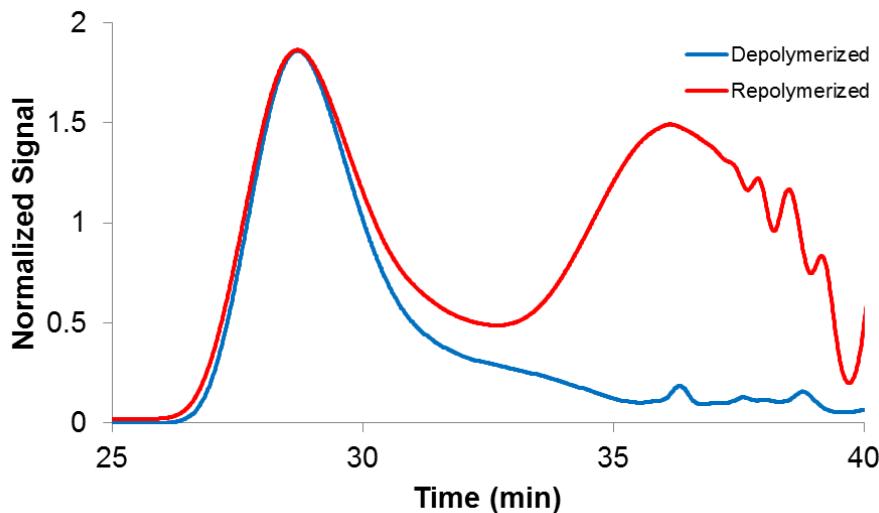


Figure 3. GPC analysis of polymer solution after sonication (blue) and after repolymerization (red).

Future Directions

We demonstrated the first case of mechanically triggered depolymerization, opening the possibilities to develop materials which can be mechanically depolymerized back to its monomers and after mass transfer repolymerized in a different needed location. We are currently studying the mechanism of this reaction, which seems to be initiated by heterolytic bond scission. These studies are being conducted by DFT calculations as well as experimental trapping of products. Furthermore, we are exploring electronic changes in the monomer, in order to develop a system which can work at higher temperatures, making it more practical to develop regenerative materials.

Sottos:

Effect of polymer chain alignment, deformation rate and relaxation on force-induced chemical reactions in an elastomer

Measurements for load, displacement, birefringence and fluorescence intensity were captured simultaneously during monotonic tensile testing using a novel optical and mechanical setup. Active PMA samples were tested at deformation rates of 0.004 s^{-1} , 0.02 s^{-1} and 0.10 s^{-1} . The resulting polymer behavior – stress, birefringence, and fluorescence intensity – are plotted in Fig 1 for representative samples at each deformation rate. The stress (Fig 1a) in the polymer samples increased with increasing deformation rate as expected for an elastomeric material. In virtually all samples, hardening was observed with increasing stretch ratio. Birefringence (Fig 1b) also increased with increasing deformation rate. Birefringence values began to plateau at all deformation rates as the chains became maximally aligned in the direction of force. The fluorescence signal, $I_{fl,raw}$, was adjusted for the number of mechanophores in the field of view and normalized by the fluorescence value at ambient equilibrium ($\lambda = 1$) fluorescence intensity. Representative normalized fluorescence, $I_{fl,norm}$, can be found in Fig 1c. For all deformation rates, rapid activation of SP (increase in $dI_{fl,norm}/d\lambda$) at large stretch ratios coincided with a plateau in the birefringence, during which polymer chains approached maximum alignment and hardening occurred. Increased birefringence and activation were considerably more apparent in the fastest testing rate (0.10 s^{-1}) when compared with middle and slowest deformation rates (0.004 s^{-1} and 0.02 s^{-1}). This finding implies that larger macroscopic stress at higher deformation

rate leads to greater chain alignment and force across the mechanophore, causing more extensive activation of SP.

Figs 2a-c reveal the trend in stretch ratio, stress, and birefringence, at the activation point, averaged over three samples at each deformation rate. The stretch value at activation, λ^* shows a marked decrease at the fastest deformation rate. The true stress, σ^* shows an increasing trend, indicating that although macroscopic stress is positively correlated to SP activation, the same macroscopic stress does not necessarily translate to the same force and activation of SP at the molecular scale. Activation birefringence, Δn^* values were similar between deformation rates, indicating that a similar degree of chain alignment was present at the onset of SP activation, regardless of the deformation rate. Finally, the rate of change of fluorescence intensity with respect to stretch ratio ($dI_{fl,norm}/d\lambda$) was averaged between stretch ratios of 8 and 9, where all samples showed an increasing fluorescence signal, but none had failed. The results plotted in Fig 2d show a clear trend of higher rate of fluorescence change (i.e. SP activation) with increasing deformation rates.

Active SP-linked PMA samples were also drawn at a deformation rate of 0.10 s^{-1} to a stretch ratio of 9 and held at constant deformation. The relaxation response of stress, birefringence and activation were measured as a function of time, as shown in Fig 3. The stress and birefringence during the constant stretch ratio stage were fitted to exponential decay curves with effective time constants (T_{eff}) of 54 s and 83 s, respectively. During stress relaxation, the fluorescence intensity in the polymer continued to increase, indicating a time dependence of force-induced chemical reactions. Although macroscopic deformation had stopped, stress in the system was sufficient to drive the reaction forward without further deformation. The fluorescence reached a maximum as the stress decayed and eventually decreased slightly over time due to the incident light source ($\lambda = 532\text{ nm}$) driving MC to SP. SP to MC activation continued to proceed forward until the stress in the sample was below ca. 10 MPa. The stress relaxation region in which normalized fluorescence intensity increased was fit to an exponential curve. The effective time constant of the fluorescence increase was 53 s – virtually the same as the stress relaxation time constant. The sample was unloaded at the same deformation rate as the loading segment by moving the load frame crossheads together until the load was reduced to zero. During unloading the fluorescence intensity decreased, indicating some reversion of the MC to SP. After returning to zero load, some fluorescence increase remained in the sample.

Effective time constants measured from stress and birefringence relaxation conditions (fitted to exponential decay for 400 s after the onset of relaxation) were between 50-100 s at all loading rates. These relaxation time scales were similar to the test time for the fastest deformation rate ($d\lambda/dt = 0.10\text{ s}^{-1}$). Slower deformation rates ($d\lambda/dt = 0.004\text{ s}^{-1}$ and $d\lambda/dt = 0.02\text{ s}^{-1}$) corresponded to test times substantially longer than the relaxation times ($t_{test} \sim 5-25 \times T_{eff}$), giving more time for polymer relaxation. The pronounced increase in stress, birefringence, and ultimately activation at the highest deformation rate is attributed to a less prominent relaxation effect over short test durations.

Fracture-Induced Mechanophore Activation

Over the past year we were able to demonstrate fracture induced mechanophore activation in spirobifluorene-linked poly(methyl methacrylate), SP-PMMA. Rubber nanoparticles were incorporated during the polymer synthesis of this material. These nanoparticles were used to increase the amount of plastic deformation ahead of the crack tip and, as a result, improve SP activation during fracture. As described in Section 1, SP activation can also be enhanced by aligning the SP molecules in the direction of applied force. Thus, prior to fracture testing, rectangular specimens, measuring $28 \times 5 \times 0.9\text{ mm}$, were pre-stretched to approximately 35% axial strain. They were subsequently tested to failure using the Single Edge Notch Tension

(SENT) test. Tests were performed on a custom-built setup that facilitated both mechanical testing and *in situ* full field fluorescence imaging. Figure 4 below shows a sequence of fluorescence images acquired during crack propagation for one specimen.

Research is now focused on investigating the use of fracture induced SP activation as a valid measure for the strain and stress fields ahead of a propagating crack. To obtain an accurate measure of the strains during testing, the Digital Image Correlation (DIC) technique is utilized. Specimens are pre-stretched as before but a speckle pattern is now applied to one side of the specimens prior to fracture testing,. The custom-built setup described earlier is modified slightly to allow for sequential DIC and fluorescence imaging. Using the data collected from the DIC images, full field strain fields are generated using the Vic-2D analysis software. An in-house Matlab script is used to produce full field stress fields based on the HRR singularity relations, the material properties and SENT test conditions. In Figure 5, contour plots of the strain field are shown alongside the fluorescence image for a specimen tested to a normalized crack length, a/W , of 0.32. Quantitative measures of the relationship between the strain and stress fields and the fluorescence intensity are currently being determined. Plots of strain, stress and fluorescence intensity as functions of distance from the crack tip will be generated and compared to ascertain how well the fluorescence intensity tracks the magnitudes and changes in strain and stress.

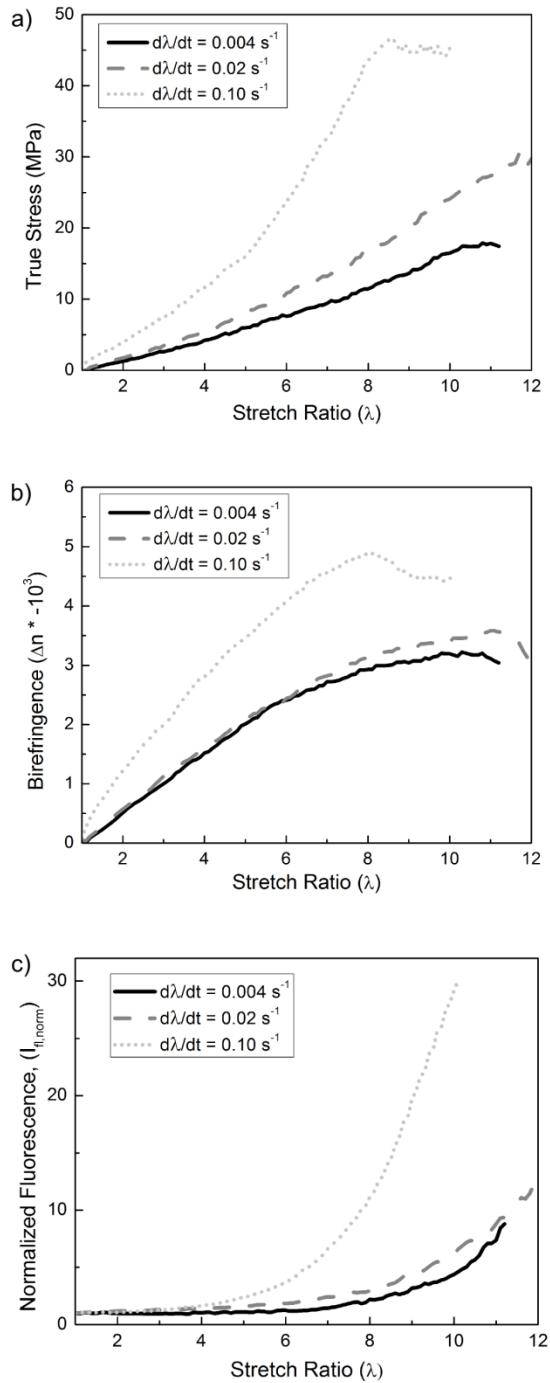


Figure 1. Representative properties of active SP-linked PMA at deformation rates ($d\lambda/dt$) of 0.004 s^{-1} , 0.02 s^{-1} and 0.10 s^{-1} . a) True stress vs. stretch ratio, b) birefringence vs. stretch ratio, and c) thickness-corrected, normalized fluorescence intensity vs. stretch ratio.

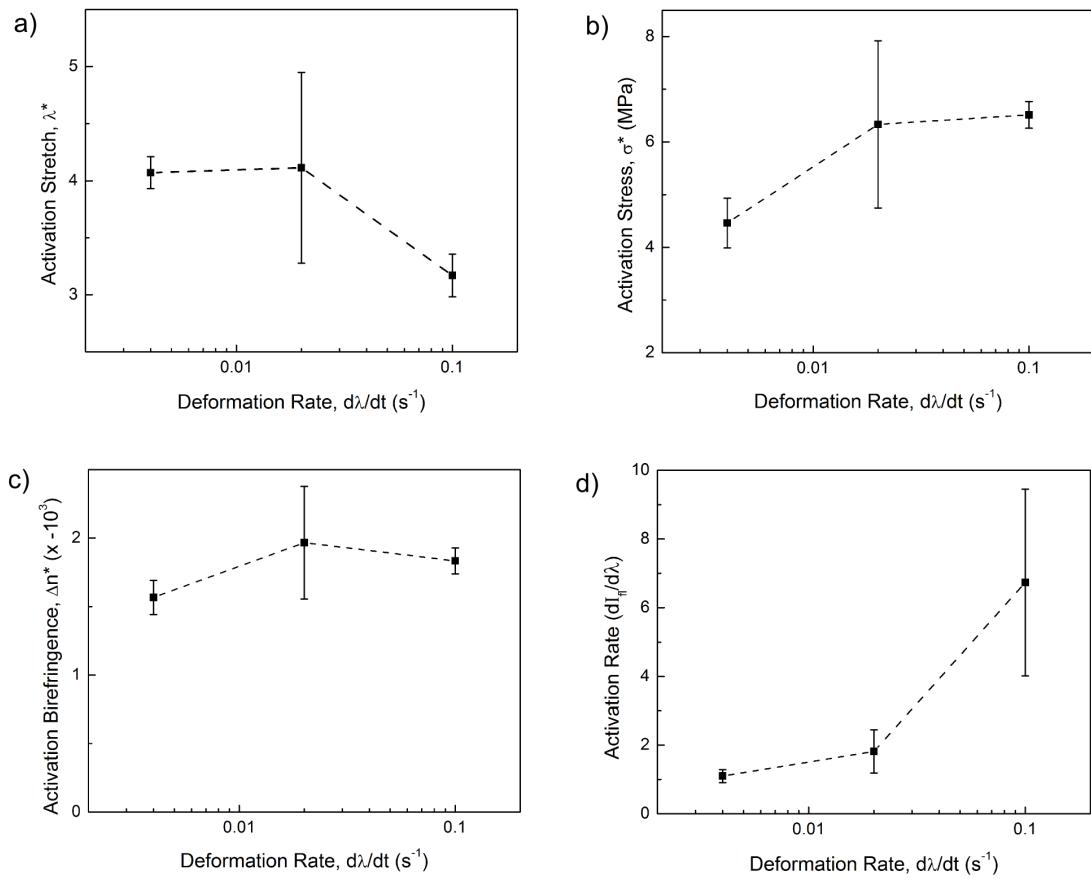


Figure 2. Activation points for SP-linked PMA as a function of deformation rate. a) Activation stretch, λ^* , (b) activation stress, σ^* , c) activation birefringence, Δn^* and d) average activation rate ($dI_{fl,norm}/d\lambda$) between $\lambda = 8$ and $\lambda = 9$.

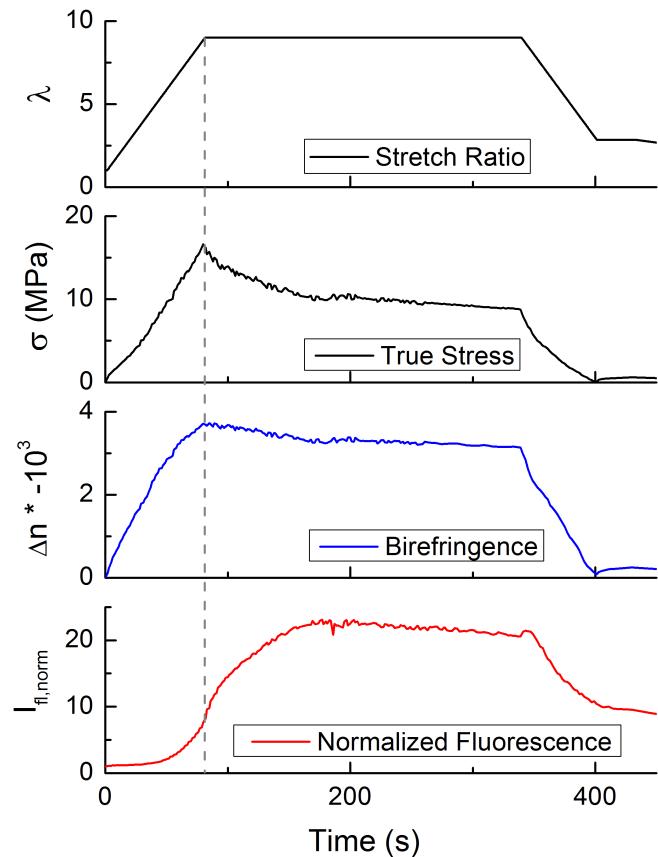


Figure 3. Stress relaxation, birefringence relaxation and activation of active SP-linked PMA loaded and unloaded at a deformation rate of 0.10 s^{-1} .

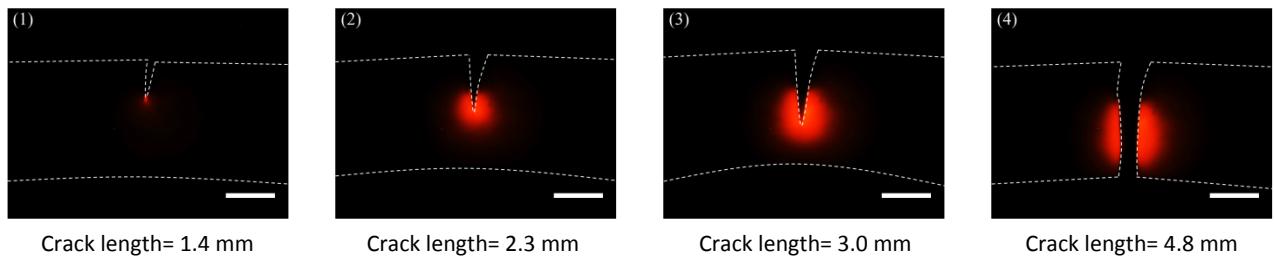


Figure 4. Fracture induced mechanophore activation. Sequence of fluorescence images of rubber toughened SP-PMMA specimen during SENT testing. Scale bar: 2 mm

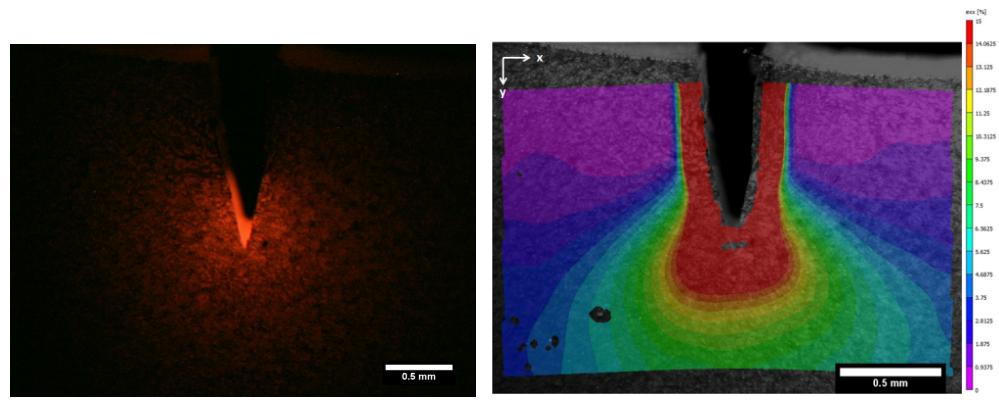


Figure 5. (a) Fluorescence image for specimen at $a/W=0.32$ (b) Corresponding strain contour plot (0 to 10%) revealing activation occurs in high strain regions (red).